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IMPROVEMENTS IN THE METHODOLOGY FOR MEASURING HYDROCHLORIC ACID IN COMBUSTION SOURCE EMISSIONS

Key Words: hydrochloric acid, combustion emissions, source sampling filters, fly ash

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ABSTRACT

In sampling gaseous hydrochloric acid in combustion source emissions by the standard method (collection of particles in a probe plug followed by absorption of gaseous HCl in an impinger solution), there is a potential for error due to interaction of HCl with the filtering medium and/or with particles on the filter. A laboratory study was conducted to examine the interaction of gaseous HCl with glass and quartz media and with particles from coal-fired and incinerator boilers. Also, some source sampling results obtained by

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different methods at cement production plants, oil-fired boilers, and a coal-fired boiler were examined. On the basis of both studies, it is recommended that sampling for gaseous HCl in combustion source emissions employ a quartz filter medium, high-velocity sample flow, minimum filter temperature, and minimum sample volume. This approach is expected to yield the most accurate HCl mass emission rates for source categories having significant chlorine in fuels or processes.

INTRODUCTION

The measurement of hydrochloric acid and total chloride ion is necessary for assessing the emissions from municipal incinerators[1] and large coal-fired boilers.[2] Sampling gaseous HCl is essential in studies that address boiler corrosion,[3] acid rain,[4] or plume reactivity.[5] For combustion sources, the accepted manual method[6] involves absorption of the gaseous HCl in a basic impinger solution (usually dilute sodium hydroxide) after removing the particulate matter with a probe plug. As in many other extractive sampling procedures, there is a potential for error due to the interaction of the gaseous component of interest with the sampling train, filtering medium, or by chemical reaction.

EPA has done extensive research on methods for measuring gaseous sulfuric acid.[7] The manner in which the sampling train is operated was found to be critical in minimizing the interaction of H_2SO_4 with particles[8] and certain filter materials. Flat filters of inert quartz were found to be best for such sampling.

The same type of interactions can occur when sampling for gaseous HCl in emissions from coal-fired boilers, cement kilns, and

municipal refuse incinerators. Most of the particles in these sources can interact with HCl due to the chemistry of fly ashes, cement dusts, or the oxides formed from burning paper in refuse. In addition, the Pyrex glass wool used routinely as a probe plug to remove particles is alkaline and could also absorb HCl. Data acquired in our source sampling program suggested that such interactions occur.[9]

As a result, a laboratory study on the interaction of gaseous HCl with different filtering media and types of particles under various conditions was undertaken. This paper reports those laboratory experiments and results, along with a limited comparison of some results of source sampling by different filtering methods. Some ways to improve the existing methodology for HCl sampling are recommended.

EXPERIMENTAL

Laboratory Studies

A laboratory HCl generator that produces a high-temperature gas stream was constructed (Fig. 1). Both the dilution and heating of cylinder HCl were done by the generator. Mass flowmeters (Hastings Model All-1K)[10] were used to deliver the desired ratios of cylinder HCl gas and cleaned compressed laboratory air to the generator. Between the pump and the filtering apparatus, gaseous HCl was collected in an impinger system containing 0.1 N NaOH. Except for establishing the HCl concentrations for a given pair of flowmeter settings, the impinger catches were discarded, since the purpose was to evaluate the interaction of filtering apparatus and gaseous HCl.

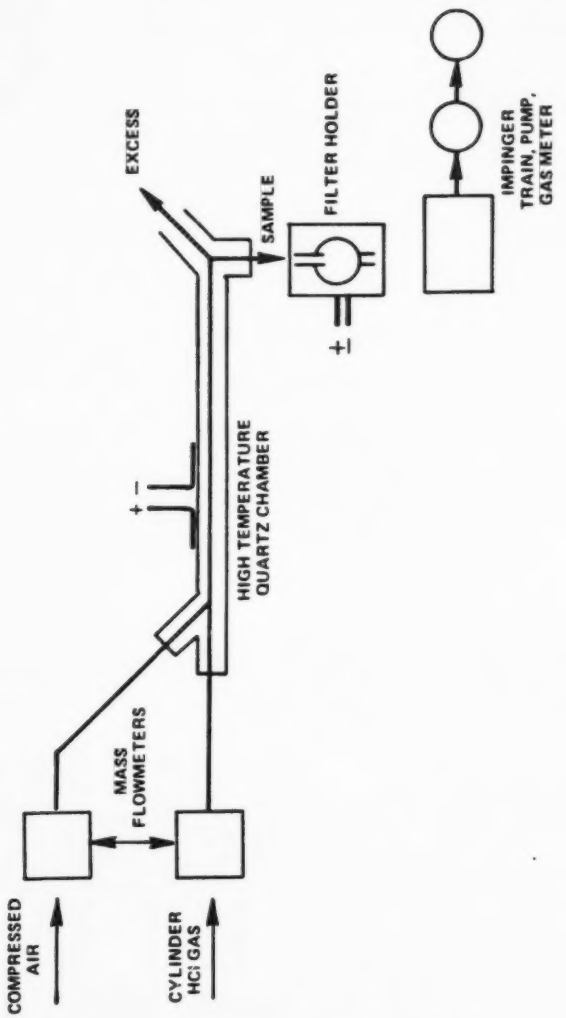

Figure 1. Gaseous Hydrochloric Acid Generator

Several experiments were conducted with glass and quartz filtering materials, some containing coal and incinerator fly ashes. The filters used were: Reeve-Angel 900 AF glass fiber filters; a high-purity quartz filter developed under EPA contract;[11] and Pyrex brand glass wool (Fisher, Catalog No. 11-388). The flat filters were 4.7 cm in diameter. The glass wool plug (approximately 0.4 g) was inserted into an 11 mm ID glass tubing and heated to simulate a sampling probe. The particles used were collected in the electrostatic precipitators (ESP's) of several different coal-fired power plants and municipal incinerators. The particle-containing filters were prepared by spreading the particles on a flat, inert surface and then pressing a preweighed filter onto these particles. The filter was then reweighed and the exposure experiments conducted. Oil-fired fly ash was not evaluated due to lack of sufficient quantity of ash.

Source Sampling

Following the laboratory investigations, a comparison was made of available sampling data from two Portland cement plants, two residual oil-fired boilers, and a coal-fired boiler. Three methods were used to acquire these data: a controlled condensation system (CCS)[12] that extracts a source sample through a high-temperature quartz probe and quartz filter; a conventional HCl sampling train (Conv.)[8] that extracts a source sample through a heated glass-lined probe with a glass wool probe plug near the inlet end of the probe; and a standard EPA particle sampling method (M-5).[13]

Analysis for Cl^-

The quantities of Cl^- in the impinger solutions, on filters, and in ash washes from laboratory studies were determined by the mercuric nitrate ($Hg(NO_3)_2$) method.[8] The Cl^- in source samples was determined using a Dionex Model 10 ion chromatograph. The Cl^- was separated using a 3 x 500 mm anion separator column in combination with a 3 x 50 mm precolumn and was quantitatively measured on the 3.0 μ mho/cm range using 0.005 M sodium borate ($Na_2B_4O_7$) as the eluant.

RESULTS

Laboratory Studies

The results of the filter media studies are shown in Table 1. With both the glass fiber filters and the glass wool plugs, a general increase with temperature in the interaction of gaseous HCl with these media occurred. The flat glass filters had a greater uptake of HCl than did the glass wool plugs. This was unexpected, since the glass filter weighs approximately 0.1 g while the glass wool plug weighs approximately 0.4 g.

In this study, the sampling rate through the filtering medium was 1 L/min for all samples. The 4.7 cm flat filter and the 1.1 cm probe plug have surface areas of 17.35 and 0.95 cm^2, respectively. At 1 L/min, the face velocity is 0.96 cm/s for the flat filter and 17.5 cm/s for the probe plug. The significantly lower face velocity for the flat glass filter could account for its increased HCl interaction relative to the glass wool plug.

TABLE 1

Absorption of Gaseous HCl by Different Filtering Media

Run	Filter Type	Gas Volume (L)	Temperature (°C)	Equivalent HCl Uptake (ppm)*
1	Flat glass	56.6	93.3	11.72
2	Flat glass	56.6	148.9	12.98
3	Flat glass	56.6	204.4	14.73
4	Flat quartz	56.6	204.4	1.10
5	Glass plug	28.3	93.3	2.60
6	Glass plug	28.3	148.9	4.00
7	Glass plug	28.3	204.4	5.90

*Equivalent HCl uptake in ppm = (mg Cl^- determined)(K) ÷ (35.453 mg Cl^-/mmol)(volume sampled in m^3), where K = proportionality constant, 24.055 m^3/mmol.

The data indicate that the glass filter has a much greater affinity for HCl than the quartz for the same sampling conditions. For the 204.4°C equivalent tests, the glass filter absorbed 14.4 times the amount of HCl absorbed by the quartz.

The results of the study on the reaction of particles from the ESP's of typical coal-fired boilers and incinerators are presented in Table 2. Two observations were made: First, very little uptake by the typical fly ashes from coal-fired ESP's was noted; second, a significant reaction between HCl and incinerator particles was

TABLE 2

Reaction of Gaseous HCl with Typical Ashes

Ash Type	Ash Weight (mg)	Temperature (°C)	Equivalent HCl Uptake (ppm)*
Coal No. 1	500.0	93.3	ND
Coal No. 1	500.2	148.9	ND
Coal No. 1	500.1	204.4	0.74
Coal No. 2	500.0	93.3	ND
Coal No. 2	500.0	148.9	1.30
Coal No. 2	500.1	204.4	2.59
Coal No. 3	498.6	93.3	ND
Coal No. 3	499.6	148.9	1.81
Coal No. 3	501.1	204.4	2.15
Coal No. 4	500.0	93.3	ND
Coal No. 4	500.0	148.9	ND
Coal No. 4	493.3	204.4	ND
Incinerator No. 1	15.38	148.9	357
Incinerator No. 2	13.27	148.9	97.0
Incinerator No. 3	10.71	148.9	79.0
Incinerator No. 4	16.45	148.9	87.0

*Calculated from the equivalents of Cl^- after subtracting amount attributed to ash and based on 28.3 L sample. ND = none detected in excess of blank.

found. With coal ashes, increased HCl uptake with an increase in temperature was observed.

A large, variable HCl-particle interaction was evident for the four different incinerator ash samples. The initial sample showed a large affinity for gaseous HCl, while the remaining three averaged 87.7 ppm uptake for the 28.3 L sample size. This large variability in uptake of gaseous HCl is likely due to the wide variability of fly ashes. These results pose serious problems when a prediction of mass emission rates of acids from such sources is needed. The fraction of the total Cl^- found in the various fractions of the sampling system using conventional filtering techniques would depend highly on both the amount and nature of the particles in the sample gas.

Source Sampling

Table 3 presents the results of the source sampling comparison in terms of front-half particulate Cl^- mass per sample volume (standard conditions). Because all of the sampling trains did not collect gaseous HCl, these concentrations are not shown. The front-half Cl^-, which is conventionally taken to be particulate Cl^-, was determined as follows: For the controlled condensation system (CCS), the probe, filter, and filter holder were rinsed with distilled H_2O, and the rinses were analyzed for Cl^-. For the conventional HCl method (Conv.), only the glass wool probe plug was washed and the rinse analyzed for Cl^-. For reference method 5 (M-5), the probe, filter, and filter holder were rinsed with distilled H_2O and the rinses analyzed for Cl^-. It was assumed that all particulate Cl^- was collected in the front half by all three methods. Any

TABLE 3

Particulate Cl^- Collected by Various Methods

Method	Source Type	Number of Measurements	Average Particulate Cl^- ($\mu g/m^3$)	Filter Temperature (°C)	Sample Velocity (cm/s)
CCS	Oil-Fired	6	1118	271	8.48
M-5	Oil-Fired	4	1066	120	6.52
CCS	Oil-Fired	8	659	271	8.55
M-5	Oil-Fired	6	751	120	10.42
CCS	Cement	4	8689	271	8.95
M-5	Cement	2	1608	120	8.93
Conv.	Cement	3	15867	121	12.76
M-5	Cement	2	127	120	7.10
Conv.	Cement	3	3468	121	13.50
CCS	Coal-Fired	4	169	271	4.60
M-5	Coal-Fired	4	85	120	6.87
Conv.	Coal-Fired	4	2068	121	3.92

additional Cl^- found in a front half that resulted in different Cl^- concentrations was then attributed to that front half having retained some gaseous HCl during sampling.

The results from oil-fired boilers show no discernible difference between the high-temperature quartz filter and the glass

fiber filter methods. While particulate Cl^- collected by CCS was greater than that collected by M-5 for the first boiler, it was less than that collected by M-5 for the second. Since the filter temperatures were equivalent for both sets of data, only the sampling velocity could have affected the results. The higher sampling velocity for the second boiler (10.42 cm/s) was the result of isokinetically sampling a sample stream of higher velocity.

The first cement plant was sampled with all three methods. The Conv. glass probe plug method collected nearly twice as much Cl^- as CCS and nearly 10 times that collected by M-5. Since the sampling velocity was greatest for the Conv. method, the higher results could be attributed to particle buildup on the plug surface during sampling.

The results from the second cement plant also show a much higher Cl^- retention (nearly 27 times) by the Conv. method than by M-5. Since both of the cement plant results -- unlike the laboratory results -- show a much higher Cl^- retention by the glass plug than by the glass filter, it is likely that it results from buildup of alkaline particles on the probe plug surface followed by absorption of gaseous HCl by those particles.

All three methods were used to sample the coal-fired boiler, and the results show a pattern similar to that of the cement plants. The laboratory studies did not show a large affinity for HCl by coal-fired particles. The significantly lower collection of Cl^- by M-5 implies that gaseous HCl was retained in the front halves of both the CCS and Conv. methods.

CONCLUSIONS

The laboratory studies indicate that both the glass filtering medium and certain particles can collect and retain gaseous HCl. In an actual sampling study, such retention would lead to erroneous attribution of the total Cl^- measured to higher-than-actual values for particulate Cl^- and lower-than-actual values for gaseous HCl.

The source sampling data indicate that particle retention of gaseous HCl could be a severe problem when sampling cement plants for HCl. Hence, the conventional method to perform HCl sampling at such sources (glass probe plug) is unacceptable.

The source sampling data also reveal a general trend of the greatest HCl retention by the glass plug method, a lesser amount by the quartz filter method, and the least by the glass filter method. This trend includes both the filter media and the particles collected during sampling. However, the laboratory results indicate that, in the absence of particles, the quartz filters retain less gaseous HCl than glass filters.

We conclude that gaseous HCl sampling should employ a quartz filter and a high-velocity sampling rate. Since there appears to be a slight increase in HCl retention as filter temperature increases, the filter temperature should be no higher than necessary. That temperature should be nominally 10 to 20°C above the water dew point of the source gas.

We further conclude that minimum sample volumes, based on detection limits of the chemical analysis method, should be used to avoid excessive particle collection on the quartz filter. This

precaution, plus the use of high-velocity sampling, should minimize any interaction between HCl and particles on the filter.

The measurement of gaseous HCl with these method improvements should result in more accurate mass emission rates of HCl for those source categories that have significant chlorine in the fuels or processes. Sampling by this recommended method was not included in the work reported here, and a field evaluation is needed.

REFERENCES

1. Rollins, R.; Homolya, J.B. Environ. Sci. Technol. 1983, 11, 1380-1383.

2. DeAngelis, D.G.; Resmik, R.B.; Ruffin, D.S.; Rigano, J.N.; McCurley, W.R.; Ochsner, J.C.; Hughes, T.W. Source Assessment: Dry Bottom Utility Boilers Firing Pulverized Bituminous Coal, EPA 600/2-79-019, U.S. Environmental Protection Agency, 1980.

3. Miller, P.D. Corrosion Studies in Municipal Incinerators, SW-72-3-3, U.S. Environmental Protection Agency, 1972.

4. Jacobsen, J.S.; Heller, L.I.; Leuken, P.V. In Proceedings of the First International Symposium on Acid Rain and the Forest Ecosystem, Battelle, Columbus, OH, 1976, p. 267.

5. Cheney, J.L.; Conner, W.D.; Bennett, R.L.; Duke, D.L.; Walters, C.L.; Knapp, K.T. Formation of a Detached Plume from a Cement Plant, Project Report, Evironmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1982.

6. Cheney, J.L.; Fortune, C.R. Sci. Total Environ. 1979, 13, 9-16.

7. Dietz, R.N. In Proceedings of Workshop on Measurement Technology and Characterization of Primary Sulfate Emissions from Combustion Sources, EPA 600/9-78-020a, U.S. Environmental Protection Agency, 1978, p. 137.

8. Cheney, J.L.; Homolya, J.B. In Proceedings of Workshop on Measurement Technology and Characterization of Primary Sulfate Emissions from Combustion Sources, EPA 600/9-78-020a, U.S. Environmental Protection Agency, 1978, p. 53.

9. Cheney, J.L.; Duke, D.L. Anal. Lett. 1983, 16(A4), 309-316.

10. Mention of brand names does not imply EPA endorsement.

11. Benson, A.L.; Levins, P.L.; Massucco, A.A.; Valentine, J.R. Development of a High Purity Filter for High Temperature Particulate Sampling and Analysis, EPA 605/2-73-032, U.S. Environmental Protection Agency, 1973.

12. Cheney, J.L. Miniature Acid Condensation System, Design and Operation, Project Report, Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1983 (in press).

13. Code of Federal Regulations, 40, Protection of the Environment, Parts 53 to 80, July 1, 1980, p. 325.

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